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<b>(54) Title:</b> MICROCAPSULES CONTAINING SUSPENSIONS OF BIOLOGICALLY ACTIVE COMPOUNDS  <b>(57) Abstract</b>  Microcapsules containing a suspension of a solid, biologically active compound in an organic, water-immiscible liquid and processes for their preparation.		

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MICROCAPSULES CONTAINING SUSPENSIONS  
OF BIOLOGICALLY ACTIVE COMPOUNDS

Field of the Invention

This invention relates to microencapsules which contain a solid biologically active compound suspended in a liquid, and processes for their preparation and for the use of such microcapsules.

Background and Prior Art

Microcapsule technology has been in existence for a number of years. Microcapsules have a variety of uses, especially for containing dyes, inks, chemical reagents, pharmaceuticals, flavoring materials, and more especially agrochemicals, that is fungicides, bactericides, insecticides, herbicides and the like.

The development and uses of microencapsulation are described by Gordon Marrs and Herbert B. Scher in Chapter 4 of "Controlled Delivery of Crop Protection Agents" (London, Taylor and Francis, 1990). As discussed by Marrs and Scher, there are three methods of forming microcapsules: i) physical methods, ii) phase separation methods and iii) interfacial polymerization.

In the third of these methods, the walls of microcapsules are generally formed of polymeric material produced by a polymerization reaction which preferably takes place at the interface between two phases, usually an aqueous phase and a water-immiscible organic phase. Thus, they may be produced from a water-in-oil emulsion or more usually an oil-in-water emulsion.

A basic patent dealing with microcapsule technology is U.S. Patent No. 4,285,720. In this patent the walls of the microcapsules are produced from polymers formed by reactions of isocyanate monomers.

A second means of forming microcapsules by interfacial polymerization is described in U.S. Patent 4,956,129. In this patent polymeric microcapsule walls are produced from etherified urea-formaldehyde prepolymers which undergo self-condensation polymerization under acid conditions.

Various improvements on these techniques have been suggested. For example, U.S. Patent 4,140,516, describes the use of phase transfer catalysts while U.S. Patent 4,448,929, describes the use of an improved protective colloid. However, in all these patents, the process have been applied only to liquids, i.e., to materials which are liquid at ambient temperature or to solutions. Unfortunately, many biologically active compounds are solids with high melting points and are not readily soluble in most commonly used solvents. The benefits of microencapsulation e.g., controlled release and increased longevity of efficacy have not been readily available to such compounds using known techniques.

It is also known to surround solids by a polymer matrix. Thus, in U.S. Patent 4,428,983, there is described a process for producing quartz crystals in a polymer matrix. The patent uses the term suspension for describing the paste of quartz crystals in the prepolymer, but this publication does not describe the production of microcapsules containing a solid suspended in a liquid.

There are a large number of publications dealing with the production and application of microencapsulated formulations of haloacetanilide herbicides. These include U.S. Patents 4,280,833; 4,417,916; 4,534,783; 4,563,212; and

4,640,709. Additionally, U.S. Patent 4,936,901 discloses herbicidal compositions which are dry flowable water-dispersible granular formulations comprising a mixture of microcapsules of a water-insoluble pesticide (including a haloacetanilide herbicide) encapsulated within a polymeric shell wall and at least one other pesticide which is nonencapsulated. Such compositions were necessary since no satisfactory techniques to produce a microcapsule containing a solid, biologically activate herbicide suspended in a liquid have been known.

It is not surprising that capsules containing a biologically active solid suspended in a liquid have not been made up until the present time since the problems to be faced in producing such a capsule are formidable. For example, in forming such capsules from an oil-in-water emulsion, the following difficulties must be addressed:

Firstly, a stable suspension of the solid in a water-immiscible liquid must be produced. If dispersants or surfactants are used, they must not interfere with further processes of dispersion used in making microcapsules.

Secondly, the suspension must be dispersed in water to produce stable, well dispersed droplets. For biologically active substances, it is preferable to have very small droplets of liquid dispersed in water to present a high surface area in the resulting microcapsules. To produce very small droplets requires high shear forces which would tend to break down the droplets and/or release the solid from suspension. Surfactants are usually required to achieve good dispersion and stable droplets.

Thirdly, the presence of one or more surfactants can make the dispersed droplet system unstable and the phenomenon of phase inversion may occur i.e., the water forms small

droplets within the liquid, a water-in-oil emulsion.

Fourthly, the solid suspended in the water-immiscible liquid is liable to migrate to the aqueous phase, particularly when emulsifying surfactants are used.

#### SUMMARY OF THE INVENTION

It has now been found that the above problems can be overcome and it is possible to produce microcapsulated compositions containing a solid biologically active compound suspended in a liquid.

#### DETAILED DESCRIPTION OF THE INVENTION

In accordance with the invention, a microencapsulated formulation of a solid biologically active compound suspended in a liquid is produced by phase separation or interfacial polymerization techniques. The preferred technique is interfacial polymerization, especially producing the capsules from an oil-in-water emulsion by procedures such as those described in U.S. Patent 4,285,720, and U.S. Patent 4,956,129, modified as described herein.

The solid, biologically active compound is preferably an agrochemical and especially a herbicide.

Preferred herbicides are s-triazines, e.g., atrazine, simazine, propazine, cyprozone;

Sulphonylureas e.g., chlorsulfuron, chlorimuron-ethyl, metsulfuron-methyl, thiameturon-methyl; and

Triketones e.g., sulcotrione.

An especially preferred herbicide is atrazine.

Another suitable compound is the fungicide (E)-methyl 2-[2-(6-(2-cyanophenoxy)pyrimidin-4-yloxy)phenyl]-3-methoxypropenoate.

The liquid in which the solid is suspended may suitably be a second herbicide, especially a thiocarbamate or a haloacetanilide and preferably acetochlor.

The haloacetanilides, particularly the subclass generally known as  $\alpha$ -chloroacetanilides, are a well-known class of herbicidal agents and have been used and proposed for use in a number of crop and non-crop applications. Some of the better known members of this class include  $\alpha$ -chloro-6'-ethyl-N-(2-methoxy-1-methylethyl)-acetanilide (metolachlor), N-butoxymethyl- $\alpha$ -chloro-2',6'-diethylacetanilide (butachlor),  $\alpha$ -chloro-2',6'-diethyl-N-methoxymethylacetanilide (alachlor), 2-chloro-N-(ethoxymethyl)-6'-ethyl-o-acetotoluidide (aceto-chlor) and  $\alpha$ -chloro-N-isopropylacetanilide (propachlor). Many other compounds of this type are disclosed in numerous patents.

The thiocarbamates are a well known class of herbicide which includes

Molinate - S-ethyl hexahydro-1H-azepine-1-carbo-thioate

Butylate - S-ethyl diisobutylthiocarbamate

EPTC - ethyl dipropylthiolcarbamate

Triallate - 2,3,3-trichloroallyl-diisopropylthiol-carbamate

Diallate - cis-1-trans-2,3-dichloroallyl-diisopropyl-thiolcarbamate

Vernolate - S-propyl dipropylthiolcarbamate

When the liquid is a herbicide, the microcapsules of the invention suitably contain 0.1-55% by weight of biologically active compounds.

The liquid may alternatively be any organic solvent which is immiscible with water, does not dissolve the biologically active solid to appreciable extent and is polar enough to dissolve the prepolymers used to form the walls of the microcapsules.

Suitable examples of such solvents are aromatic compounds such as xylenes or naphthalenes, especially Solvesso 200; aliphatic compound such as alkyl esters, especially alkyl acetates, e.g., Exxate 700 - Exxate 1000; alkyl phthalates, such as diethyl phthalate, dibutylphthalate; alcohols, such as isopropyl alcohol; ketones, such as acetophenone, cyclohexanone. The solvent may be a mixture of more than one compound.

A safener for either herbicide may be present and many such safeners or antidotes as well known in the art. Preferred types for use with haloacetanilide herbicides include dichloroacetamides such as dichlormid (N,N-diallyl dichloroacetamide); 2,2,5-trimethyl-3-dichloroacetyl oxazolidine (R-29148), N-dichloroacetyl-1-oxa-4-azaspiro[4,5]decane (AD-67); 4-dichloroacetyl-2,3-dihydro-3-methyl-1,4-benzoxazine (CGA-154281); 1-(dichloroacetyl)hexahydro-3,3,8a-trimethylpyrrolo-[1,2-a]-pyrimidin-6(2H)-one and N-(1,3-dioxolan-2-yl-methyl)-N-(2-propenyl)-2,2-dichloroacetamide (PPG-1292).

These and other dichloroacetamides are described, for instance, in U.S. Patents 4,124,372; 4,256,481; 4,294,764; 4,448,960; 4,601,745; 4,618,361; 4,708,735 and 4,900,350. Additional known types of safeners or antidotes include certain oxime derivatives (U.S. Patents 4,070,389 and 4,269,775, for instance), thiazole carboxylic acids and derivatives (U.S. Patent 4,199,506 for instance), haloacyltetrahydroisoquinolines (U.S. Patent 4,755,218, for example), aryl cyclopropane carbonitriles (U.S. Patent 4,859,232, for example) and 1,8-naphthalic acid, its anhydride and derivatives.



Safeners or antidotes, when included, will usually be contained in the organic or water-immiscible phase.

The preferred materials for the microcapsule is a polyurea, formed as described in U.S. Patent 4,285,720, or a urea-formaldehyde polymer as described in U.S. Patent 4,956,129. The polyurea is especially preferred.

In brief, the process comprises the following steps.

Step 1. Producing the solid biologically active material with the required particle size, suitably by a milling process. The preferred average particle size of the solid is 0.01-50 microns, preferably 1-10 microns and even more preferably 1-5 microns.

Step 2. Suspending the solid biologically active material in an organic liquid. The liquid is preferably a poor solvent for the solid, that is it will not dissolve large quantities of the solid. The liquid must also be immiscible with water, but polar enough to dissolve the prepolymers used in the microencapsulation process.

The liquid preferably contains a dispersant capable of keeping the solid in the liquid but which does not allow the solid to be extracted into the water when the suspension is dispersed into water. In addition, when the suspension is added to water, the dispersant must not allow phase inversion to occur i.e., the water must not be allowed to be taken into an emulsion by the organic liquid.

The exact choice of dispersants will depend on the choice of solid and the liquid but preferred dispersants are non-ionic surfactants which act by steric hindrance and are active only at the solid/organic liquid interface and do not act as emulsifying agents. Such dispersants are suitably made

up of i) a polymeric chain having a strong affinity for the liquid and ii) a group which will absorb strongly to the solid.

Examples of such dispersants are Hypermer PS1, Hypermer PS2, Hypermer PS3 and Hypermer LP2; Atlox LP1, Atlox LP2, Atlox LP4, Atlox LP5, Atlox LP6, Atlox PS2 and Atlox PS3 available from ICI Americas Inc., Wilmington, Delaware; and Agrimer polymers from GAF, e.g., Agrimer AL-220, Agrimer AL-216.

In general, the range of dispersant concentration used is from about 0.01 to about 10% by weight based on the organic phase, but higher concentration of surfactant may also be used.

Alternatively, the procedures of Steps 1 and 2 may be varied by preforming a milling process, to reduce the particle size of the solid, after the solid biologically active material is suspended in the organic liquid (media milling).

Step 3: A physical dispersion of a water-immiscible phase in an aqueous phase is prepared. To obtain the appropriate dispersion, the organic phase is added to the aqueous phase, with stirring. A suitable dispersing means is employed to disperse the organic phase in the liquid phase. The means may be any high shear device, so as to obtain a desired droplet (and corresponding microcapsule particle) size within the range of from about 1 to about 200 microns. Preferably the droplet size is from about 1 to about 30 microns, most preferably from about 3 to about 20 microns, average. Once the proper droplet size is obtained, the dispersion means is discontinued. Only mild agitation is required for the remainder of the process. The water-immiscible phase comprises the solid, biologically active compound suspended in

the liquid to be encapsulated prepared as described above in Steps 1 and 2. The aqueous phase is comprised of water and a material termed a "protective colloid". Preferably it further contains a surfactant.

In general, the surfactant or surfactants in this phase may be anionic or non-ionic surfactants with an HLB range of from about 12 to about 16 that is high enough to form a stable oil-in-water emulsion. If more than one surfactant is used, the individual surfactants may have values lower than 12 or higher than 16. However, when combined together the overall HLB value of the surfactants will be in the range 12-16. Suitable surfactants include polyethylene glycol ethers of linear alcohols, ethoxylated nonylphenols, naphthalene sulfonates, and the like. Other suitable surfactants include block copolymers of propylene oxide and ethylene oxide and anionic/nonionic blends. Preferably the hydrophobic portion of the surfactant has chemical characteristics similar to the organic liquid. Thus, when the organic liquid is an aromatic solvent, the surfactant would suitably be an ethoxylated nonphenol.

Especially preferred surfactants are Tergitol NP7, Tergitol NP40 and Tergitol 15-S-20.

In general, the range of surfactant concentration in the process is from about 0.01 to about 10.0 percent by weight, based on the aqueous phase, but higher concentrations of factant may also be used.

The protective colloid present in the aqueous (or continuous) phase must absorb strongly onto the surface of the oil droplets. Suitable colloid forming materials include one or more of polyalkylates, methyl cellulose, polyvinyl alcohol, polyacrylamide, poly(methylvinyl ether/maleic anhydride), graft copolymers of polyvinyl alcohol and methylvinyl ether/

maleic acid (hydrolyzed methylvinyl ether/maleic anhydride; see U.S. Patent 4,448,929, which is hereby incorporated by reference herein), and alkali metal or alkaline earth metal lignosulfonates. Preferably, however, the protective colloid is selected from alkali metal and alkaline earth metal lignosulfonates, most preferably sodium lignosulfonates. Especially preferred colloids also contain polyvinyl alcohol.

There must be sufficient colloid present to afford complete coverage of the surfaces of all the droplets of the organic liquid. The amount of protective colloid employed will depend on various factors, such as molecular weight, compatibility, etc. The protective colloid can be added to the aqueous phase prior to the addition of the organic phase, or can be added to the overall system after the addition of the organic phase or the dispersion of it. The protective colloid is generally present in the aqueous phase in an amount of from about 0.1 to about 10.0 percent by weight.

Any surfactant used in the aqueous phase must not displace the protective colloid from the surface of the droplets of organic liquid.

If the water-immiscible liquid is a thiocarbamate or a haloacetanilide herbicide, then depending on the intended application or use of this microencapsulated product, the compositions of this invention may also include a herbicide safener or antidote.

Safeners or antidotes, when included, will usually be contained in the organic or water-immiscible phase.

The preferred average particle size of the droplets of the water-immiscible liquid containing a biologically active solid is 1-200 microns, preferably 1-30 microns and more preferably 3-20 microns. Particle size can be adjusted

according to the end use of the microcapsules by adjusting stirring speed and time, and by the choice of surfactants and the amount of surfactants employed.

In order to obtain the microcapsules, the organic liquid and/or the water must contain one or more materials which can react to form a polymer at the interface between the organic liquid and the water.

In the process described in U.S. Patent 4,285,720, polyisocyanates are dissolved in the organic phase (i.e., at Step 2 in the above procedure) and polymerization takes place by hydrolysis of the prepolymers at the water/organic liquid interface to form amines which, in turn, react with unhydrolyzed monomers to form the polyurea microcapsule wall. A single compound or a mixture of two or more polyisocyanates may be used. Mixtures are preferred. Of the polyisocyanates, polymethylene polyphenylisocyanate (PAPI), and isomeric mixtures of toluene diisocyanate (TDI) are preferred. Particularly preferred are mixtures of polymethylene polyphenylisocyanate with isomeric mixtures of toluene diisocyanate, in a weight ratio of PAPI:TDI of from about 1:30 to about 4:1, especially 1:10 to 1:1.

The amount of the organic polyisocyanate used in the process will determine the wall content of the microcapsules formed. In general, the polyisocyanate (or microcapsule wall formed from it) will comprise from about 2.0 to about 75.0 percent by weight of the microcapsule. Most preferably the wall will comprise from about 4 to about 15% by weight, of the microcapsule.

The dispersion is maintained in a temperature range of from about 20°C to about 90°C preferably 40°- 60°C during which the condensation reaction takes place to form the polyurea, at the interfaces between the droplets of the organic phase and the aqueous phase.

A thiocarbamate or a haloacetanilide herbicide may be used as a solvent for the polyisocyanates. Alternatively, solvents such as xylene may be used (see Canadian Patent 1,094,402).

Another suitable system for forming microcapsules is described in U.S. 4,956,129, in which the polymer is formed from an etherified urea-formaldehyde prepolymer in which 50-98% of the methylol groups have been etherified with a  $C_4-C_{10}$  alcohol. Self-condensation of the prepolymer takes place under the action of heat at low pH.

To form the microcapsules, the temperature of the two-phase mixture is raised to a value of from about 20°C to about 90°C, preferably from about 40°C to about 90°C, most preferably from about 40°C to about 60°C. Depending on the system, the pH value may be adjusted to an appropriate level.

The following are examples of preparations of compositions of this invention.

#### GENERAL PROCEDURE

In the first two examples which follow, the compositions were prepared by the following general procedure:

The organic phase was added to the aqueous phase, and an oil-in-water emulsion was formed by means of a high shear stirrer. The average particle size was in the range of  $11.0 \pm 2$  microns. While mild agitation was maintained, the temperature of the batch was raised to 50°C over a period of 30 minutes, and held at 50°C for 3 hours. The resulting microcapsule suspension was then allowed to cool to room temperature. The additional ingredients were then added and the pH was then adjusted to 11.0 with 50% caustic.

-13-

In the third example, the pH of the aqueous phase was adjusted to 2.0. Then the organic phase was added to the aqueous phase, and an oil-in-water emulsion was formed by means of high shear stirrer. The average particle size was in the range of  $28 \pm 3$  microns. While mild agitation was maintained, the temperature of the batch was raised to 50°C over a period of 30 minutes and held at 50°C for 3 hours. The resulting microcapsule suspension was then allowed to cool to room temperature. The additional ingredients were then added and the pH was adjusted to 7.0 with 50% caustic.

EXAMPLE I 14473-27-1

A composition was prepared using the general procedure described above with the following ingredients.

<u>Component</u>	<u>Weight, g.</u>	<u>Weight %</u>
ORGANIC PHASE		
Atrazine (technical grade)	65.0	16.58
Acetochlor (technical grade)	100.0	25.51
N,N-diallyldichloroacetamide	17.0	4.33
Hypermer LP5	9.0	2.30
Hypermer LP1	4.0	1.02
Polymethylene polyphenylisocyanate	2.0	0.51
Toluene diisocyanate	9.0	2.29
AQUEOUS PHASE		
Reax 100M (sodium salt of ligno-sulfonic acid, 40% solution in water)	18.0	4.59
Gelvitol 40/10 (PVA, 20% solution in water)	18.0	4.59
Tergitol NP7 (20% solution in water)	4.0	1.02
Tergitol NP40 (70% solution in water)	1.0	0.26
Water	138.8	35.15

-14-

## ADDITIONAL INGREDIENTS

Attapulgate (attagel 40) <sup>1</sup>	3.8	0.98
Xanthan gum (Kelzan) <sup>2</sup>	0.3	0.07
Sodium carbonate <sup>3</sup>	2.7	0.70
Proxel GXL	0.4	0.10

TOTAL

393.0

100.00

The resulting microencapsulated product had an average particle diameter of 10.0 microns.

- <sup>1</sup> = suspending agent  
<sup>2</sup> = buffering agent  
<sup>3</sup> = biocide

EXAMPLE II 14585-26

A composition was prepared using the general procedure described above with the following ingredients.

<u>Component</u>	<u>Weight, g.</u>	<u>Weight %</u>
ORGANIC PHASE		
2-(2-nitro-4-methanesulfonyl-benzoyl)-1,3-cyclohexanedione	50.0	12.50
Solvesso 200	115.0	28.75
Hypermer LP6 (40% solution in hydrocarbons)	32.0	8.00
Polymethylene polyphenylisocyanate	8.0	2.00
Toluene diisocyanate	8.0	2.00
AQUEOUS PHASE		
Reax 100M (sodium of lignosulfonic acid, 40% solution in water)	18.0	4.50
Gelvatol 40/10 (PVA, 20% solution in water)	18.0	4.50
Tergitol NP7 (20% solution in water)	4.0	1.00
Tergitol NP40 (70% solution in water)	1.0	0.25
Water	138.8	34.70



-15-

## ADDITIONAL INGREDIENTS

Attapulgate (attagel 40)	3.8	0.95
Xanthan gum (Kelzan)	0.3	0.07
Sodium carbonate	2.7	0.68
Proxel GXL	0.4	0.10

		=====	=====
TOTAL	400.0	100.00	

The resulting microencapsulated product had an average particle diameter of 12.5 microns.

EXAMPLE III 14369-21-3

A composition was prepared using the general procedure described above with the following ingredients.

<u>Component</u>	<u>Weight, g.</u>	<u>Weight %</u>
ORGANIC PHASE		
Atrazine (technical grade)	39.8	10.00
Solvesso 200	92.7	23.28
Beetle 1050 Resin (butylated urea-formaldehyde prepolymer, 60% solution in butanol)	26.6	6.68
AQUEOUS PHASE		
Petro BAF (sodium dialkylnaphthalen- sulfonate)	0.8	0.20
Reax 100M (sodium salt of ligno- sulfonic acid, 40% solution in water)	18.8	4.72
Water	215.0	53.99

-16-

## ADDITIONAL INGREDIENTS

Attapulgate (attagel 40)	3.8	0.95
Xanthan gum (Kelzan)	0.3	0.08
Proxel GXL     0.4   0.10		

		=====	=====
TOTAL	398.2	100.00	

The resulting microencapsulated product had an average particle diameter of 28 microns.

In each Example the final product of the process was analyzed by microscopy and polarography. The results showed that the suspension of biologically active solid was successfully microencapsulated and the aqueous phase was substantially free of the solid.

## WHAT IS CLAIMED IS:

1. A microcapsule containing a solid biologically active compound suspended in a liquid.
2. A microcapsule according to Claim 1 wherein the liquid is a water-immiscible liquid.
3. A microcapsule according to claim 1 or 2 wherein the biologically active compound is an agrochemical.
4. A microcapsule according to any of claims 1-3 wherein the agrochemical is a herbicide.
5. A microcapsule according to claim 4 wherein the herbicide is atrazine.
6. A microcapsule according to any of claims 1-5 wherein the liquid is a biologically active compound.
7. A microcapsule according to claim 6 wherein the liquid is a herbicide.
8. A microcapsule according to claim 7 wherein the liquid herbicide is a haloacetanilide or a thiocarbamate.
9. A microcapsule according to claim 8 wherein the liquid herbicide is acetochlor.
10. A microcapsule according to any of claims 7-9 wherein a herbicide safener is also present in the microcapsule.
11. A microcapsule according to any of claims 1-10 in which a polyurea capsule is formed from isocyanate monomers.

12. A microcapsule according to claim 11 in which the isocyanate monomer is a mixture of polymethylene polyphenylisocyanate and an isomeric mixture of toluene diisocyanate.

13. A microcapsule according to claim 1 containing from about 0.1 to about 55 weight percent of biologically active compounds.

14. A microcapsule according to claim 1 in which the capsule is formed from a urea-formaldehyde prepolymer.

15. A microcapsule according to claim 14 in which the urea-formaldehyde polymer is produced from an etherified urea-formaldehyde prepolymer in which from about 50% to about 98% of the methylol groups of the said prepolymer have been etherified with a C<sub>4</sub>-C<sub>10</sub> alcohol.

16. A microcapsule according to any of claims 11-15 in which the polymer comprises from about 4 to about 15% by weight of the capsule.

17. A process for preparing microcapsules containing a solid, biologically active compound suspended in liquid which process comprises:

a) preparing a suspension of said compound in an organic liquid which is immiscible with water by either:

i) producing a powder of said compound with a particle size of 0.01-50 microns and suspending said powder in said organic liquid, or

ii) suspending said compound in said organic liquid and media milling said compound to a particle size of 0.01-50 microns;

b) introducing said suspension into water containing a protective colloid and optionally a surfactant capable of maintaining the organic liquid as droplets in the water without extracting the solid from the organic liquid into the water; the organic liquid and/or the water containing in solution one or more monomers or prepolymers which can react to form a polymer at the interface of the organic liquid and water;

c) mixing the suspension of organic liquid in the aqueous phase under high shear to form an oil-in-water emulsion; and

d) adjusting as necessary the temperature and/or pH of the oil-in-water emulsion such that a polymerization reaction taken place to form the microcapsules.

18. A process according to claim 17 wherein the particle size of the biologically active solid is 1-10 microns.

19. A process according to claim 17 or 18 wherein the particle size of the droplets of organic liquid after dispersion in the water is 1-30 microns.

20. A process according to any of claims 17-19 in which the protective colloid is an alkaline metal or alkaline earth metal lignosulfonate and optionally also contains polyvinyl alcohol.

21. A process according to any of claims 17-20 in which the surfactant in the aqueous phase has an HLB value of 12-16.

22. A process according to any of claims 17-21 wherein the prepolymer is an organic polyisocyanate dissolved

in the organic liquid which when heated forms a polyurea by hydrolysis of an isocyanate to an amine which in turn reacts with another isocyanate to form the polyurea.

23. A process according to claim 22 in which the polyisocyanate is a mixture of polymethylene polyphenylisocyanate and an isomeric mixture of toluene diisocyanate.

24. A process according to any of claims 17-23 in which the organic liquid contains a dispersant active only at the solid/organic liquid interface and which does not act as an emulsifying agent.

25. A process according to any of claims 17-24 wherein the prepolymer is a urea-formaldehyde prepolymer in which about 50-98% of the methylol groups have been etherified with a C<sub>4</sub>-C<sub>10</sub> alcohol, and which forms a solid polymer at pH 0-4 at 20-100°C.

## INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 94/02440

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 A01N25/28 A01N43/70 A01N41/10 //(A01N43/70, 37:26, 25:28),  
(A01N41/10, 25:28)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	GB,A,2 011 341 (PHILAGRO) 11 July 1979  see page 1, line 3 - line 4 see page 2, line 9 - line 24 see page 3, line 39 - line 44 see page 3, line 50 - line 58 see page 3, line 64 - page 4, line 1 see page 9; example 8 ---	1-4, 11, 13, 16-19
X	US,A,4 722 838 (S.TOCKER) 2 February 1988  see column 2, line 49 - line 59 see column 3, line 54 - line 63 see column 4, line 20 - line 35 see column 7; example 5 --- -/--	1-4, 13, 16, 18, 21

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

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 "E" earlier document but published on or after the international filing date  
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 "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention  
 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone  
 "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.  
 "&" document member of the same patent family

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9 March 1995

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Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax (+31-70) 340-3016

Authorized officer

Lamers, W

## INTERNATIONAL SEARCH REPORT

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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